

Micellar-enhanced ultrafiltration of phenol by means of oxyethylated fatty acid methyl esters

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Abstract

The optimized application of micellar-enhanced ultrafiltration (MEUF) in industrial scale requires the ability to develop simulation models. The more conventional approach for the description of relationships between operation conditions like, for example, surfactant concentration and separation performance and fouling, centers on the evaluation of overall resistance and time-independent relationships between concentrations before and after the membrane. In this paper, a novel approach is presented. It is based in the evaluation of relationships between averaged resistance and permeation fluxes, and a molar ratio pollutant/surfactant to predict the efficiency of the separation. The evolution of the additional resistance to permeation generated by the deposition of surfactant on the membrane is described as a sequence of: a maximum initial resistance due to gelification; a decrease in the resistance, apparently connected with the deformation of the surfactant gel by the permeating flux; and an aging effect. It is observed that different pollutants have different effects on the initial resistance and its evolution. In the case of phenol, higher concentration causes an increase of the initial resistance. It does not seem to have an effect on the aging rate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ultrafiltration; Modeling; Surfactant; Oxyethylated methyl dodecanoate; Separation; Phenol; Nitrophenol

1. Introduction

The modeling of a separation process demands a set of equations capable to describe the various factors involved in the process, and give a prediction of the separation efficiency. In the case of semi-continuous processes, it also demands the ability to predict the effective operation time. In all the separation processes using membranes, fouling is a major concern. It has a more marked effect in membranes with smaller pore sizes. Not only fouling is more troublesome, but also

larger capital and operation costs are required for the operation [1]. Therefore, it is reasonable to try to find techniques for the separation of a given kind of particles/molecules with larger pore-sized membranes than expected. Ultrafiltration is a membrane separation process aimed at dissolved/dispersed particles of a size ranging from 1 to 100 nm. As a consequence, the pore size is too large to reject small molecules below 10 000 Da, which would require nanofiltration. However, for several years now research has been performed on the use of surfactant micelles to increase the ability of ultrafiltration membranes to separate such small molecules or ions. The technique takes advantage of the principle that micelles (aggregates of surfactant molecules of sizes above 10 nm)

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Nomenclature

C	concentration (g l^{-1})
K	characteristic permeation coefficient ($\text{m}^3 \text{atm}^{-1} \text{s}^{-2}$)
P	pressure (atm)
R	resistance ($\text{atm cm}^{-1} \text{s}$)
v	permeation flux (cm s^{-1})

Greek symbols

Φ	weight ratio between bound pollutant and binding (micellar) surfactant (non-dimensional)
μ	viscosity ($\text{m}^2 \text{s}^{-1}$)

Superscripts

per	permeate
ret	retentate

Subscripts

m-s	relative to the surfactant secondary layer
mem	relative to the membrane
PH	Phenol
W	water
A	solvent (water)

are rejected by ultrafiltration membranes, and in the process any solutes dissolved inside of the micellar cores or bound to their surfaces are also rejected.

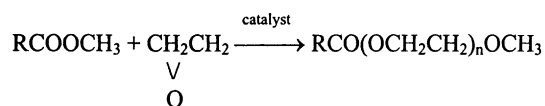
Applications of the technique, called micellar-enhanced ultrafiltration (MEUF) can be classified within two groups: separations due to binding of solute ions onto the surface of micelles [2–4], and separation of solute ions and molecules due to solubilisation into micelles. In the latter case, there are still two main options. Solubilisation of a solute into the core of micelles or in the hydrophilic mantle [5–7] and extraction of a hydrophilic species by complexation with a complexants [8–13]. In general, chelation into micelles of heavy metal ions or solubilisation into the micelles of molecules with hydrophobic affinity (like phenols) are considered more promising than surface binding MEUF variants.

MEUF has several characteristics: (1) due to membrane polarization effects, a secondary layer of surfactant in liquid-crystalline form deposits onto the

membrane surface [14,15]; (2) the secondary layer “fouls” the membrane, reducing its permeability; (3) it enhances the ability of the membrane to reject the target solute; (4) the permeate contains unbound solute and usually monomeric surfactant, although this statement is not true at very high surfactant concentrations in the feed upstream the membrane [16]; (5) a maximum permeation flux is reached after some time, and thereafter the permeation flux slows down. MEUF may achieve rejections in excess of 90%, but typically the retentate (which contains the concentrated solutes and solute-removing surfactants) may still be about one fifth in volume of the original solution [9]. Further concentration may reach to the point where micellar surfactant starts crossing the membrane. Nevertheless, the quality of the permeate improves significantly when compared with the starting solution.

The aim of this work is to study the resistance and permeation flux for micellar solutions of oxyethylated methyl dodecanoate of various hydrophobicity.

The studied surfactants can be considered as models of new prospective non-ionic surfactants which can be obtained by direct reaction of methyl esters of fatty acids with ethylene oxide in the presence of appropriate catalysts [17–20].



These surfactants may soon find several applications including detergents, as they are obtained from intermediate methyl esters without converting them to fatty alcohols and then to traditional alcohol oxyethylates.

2. Theory

The flux through membranes is described by the Darcy’s law:

$$v_A = \frac{\Delta P}{\mu_W / K_{\text{mem}}} \quad (1)$$

that assumes that the resistance to permeation is connected with the viscosity of the solution and a membrane constant. Both series resistance models and thermodynamics of irreversible processes (TIP) models are used to describe MEUF. TIP associates the flux

through the membrane with the variation of thermodynamic properties across the membrane [21]. This phenomenological approach has allowed observing that the overall membrane resistance during MEUF has an hyperbolic dependence of the feed surfactant concentration. Azoug [16] reported that as it could be expected, permeation of water follows Eq. (1), with an approximately constant resistance, while the resistance opposed to permeation of submicellar surfactant solutions has a strong dependence with the surfactant concentration which can be associated with changes in the liquid viscosity. They also observed that surfactant solutions containing spherical micelles cause a strong resistance of the membrane, with a small functional dependence of the micellar surfactant concentration, while surfactant solutions with highly structured micelles (e.g. rod-like) cause an even stronger resistance from the membrane, with a higher functional dependence of the micellar surfactant concentration. TIP allowed the authors to explain the functional dependency of the overall resistance to permeation with surfactant concentration. In the presence of rod-like micelles, the surfactant concentration in the permeate is above the cmc: while in solutions with spherical micelles only monomeric surfactant may permeate, at high enough concentrations the dynamics of the process make possible that the surfactant in the permeate contains micelles. While TIP provides very useful information of the effect of the various properties on the performance of the system, from an engineering point of view resistance models seems more convenient, and have the advantage of allowing the isolation of the phenomenon of resistance to permeation due to the gelation process, whereas TIP provides averaged models extended to all the membrane.

If an additional resistance term must be considered to account for the effect of the secondary layer, Eq. (1) may be expanded to

$$v_A = \frac{\Delta P}{(\mu/K_{\text{mem}}) + R_{\text{SL}}} \quad (2)$$

where R_{SL} is the resistance presented by the secondary layer. For the case of a secondary layer generated by a non-ionic surfactant, where the electrostatic effects due to split between surfactant concentration profile and counterion concentration profile do not exist (these affect anionic and cationic surfactants), the membrane polarization effect may be reduced to

the balance between friction of the water flux going through the membrane and the diffusional driving force opposing it, and due to the concentration gradient between the membrane surface and the bulk of the upstream feed. Therefore, gelification of the surfactant should take place at a greater extent if the polarization is stronger. In the case of non-ionic surfactants, polarization should be stronger at higher feed concentrations or under higher permeation flux rates. Thus, the growth of the thickness of the secondary layer may be described by

$$\frac{d\delta}{dt} = V_{\text{TF}} r_{\text{LD}} \frac{V_m}{S_{\text{mem}}} = r_{\text{LD}} \frac{V_m}{\delta_{\text{TF}}} \quad (3)$$

where δ is the thickness of the secondary layer, r_{LD} the average reaction rate for deposition of gelified surfactant onto the membrane, V_m the apparent molar volume of the solute, V_{TF} the volume of the thin film adjacent to the secondary layer which is considered in this analysis as the reaction volume for the gelification reaction and S_{mem} is the surface of the membrane over which deposition is taking place. With the flux defined as a function of permeability as

$$J = \frac{p}{\delta} \Delta P \quad (4)$$

from where the resistance can be alternatively defined as $R = \delta/p$. The increase in resistance due to the thickening of the secondary layer and changes in its permeability will, therefore, be

$$\frac{dR}{dt} = \frac{r_{\text{LD}}}{p} \frac{V_m}{\delta_{\text{TF}}} + \delta \frac{d(1/p)}{dt} \quad (5)$$

where p is the permeability of the secondary layer. Let us make the arbitrary assumption of the gelification reaction being first order (function of the surfactant concentration) with the form $r_{\text{LD}} = K_{\text{dep}} C_{\text{surf}}$, and assume that we can average the rate of deposition in the thin film taking the concentration value at both ends of the thin film as C_{feed} at the end opposite to the membrane and next to the membrane is $C_{\text{feed}} \exp(\Delta\mu/RT)$ where $\Delta\mu$ is the gradient of chemical potential for the surfactant across the thin film. Applying a simplified linear Maxwell–Stefan model [22], the concentration next to the membrane becomes $C_{\text{feed}} \exp((\delta_{\text{TF}} v_A)/D_{\text{AB}})$. This is done assuming a “sphere in liquid” model to the diffusion of the surfactant across the thin film. This relates

the chemical potential gradient to the solvent–solute frictional drag in a stationary state through the equation $\Delta\mu/RT = (v_A - v_B)\delta_{TF}/D_{AB}$. Here v_A is the velocity at which the solvent (water) flows across the thin film, the surfactant velocity v_B is taken as zero because the surfactant concentration gradient in the thin film may be considered stationary, and D_{AB} is the Maxwell–Stefan diffusivity coefficient. Replacing in Eq. (5) the variable r_{LD} for an expression explicitly dependent on the effect of the friction of the water flux on the average surfactant concentration in the thin film, we obtain the expression

$$\frac{dR}{dt} = \frac{k_{dep}}{p} \frac{V_m}{2\delta_{TF}} C_{feed} \left(1 + \exp\left(\frac{\delta_{TF}}{D_{AB}} v_A\right) \right) + \delta \frac{d(1/p)}{dt} \quad (6)$$

The expression tells us that at higher flux rates the first term of the right hand will be larger (the resistance will raise faster). This obviously means that the flux would subsequently drop also faster. The second term of the right hand describes the variation with time of the resistance due to temporal changes of permeability of the secondary layer.

3. Experimental

3.1. Chemicals

Four homologue oxyethylated methyl dodecanoates with average oxyethylation degrees 7, 9, 11 and 14, designated from now on as EO n , with n being the average ethoxylation degree were tested. The surfactants were synthesized using calcium-based W7TM catalyst [23,24]. The composition of the products is typical for narrow range distributed oxyethylates and their composition was determined by GC and HPLC chromatographic methods [25] (Fig. 1).

Phenol (pure), abbreviated as PH, was supplied by LOBA CHEMIE, Austria and 4-nitrophenol (pure), abbreviated as NPH, was supplied by POCh, Gliwice, Poland.

3.2. Ultrafiltration

Ultrafiltration was carried out at room temperature in a 10 ml Amicon 8010 stirred cell. The nitrogen

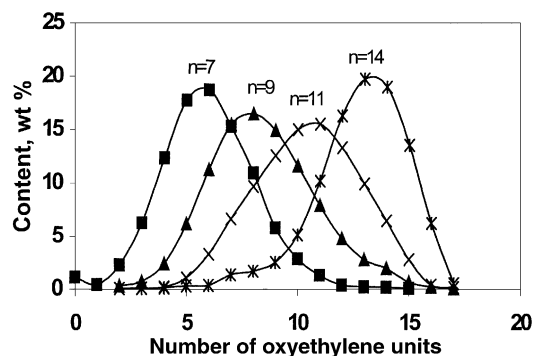


Fig. 1. Composition of oxyethylated methyl dodecanoate.

pressure was 0.35 MPa. Membranes were hydrophilic PLGC-type Millipore membranes made from regenerated cellulose with a molecular weight cut-off of 10 000 Da. Membrane filtration surface was 4.1 cm². Equal volumes (5 ml of each) of phenol solution and surfactant solutions with the surfactant concentration equal to 20, 100, 200 or 400 cmc were introduced into the filtration module and after 5 min of mixing the filtration was started keeping vigorous mixing. The cmc for each surfactant had been determined in distilled water and were 7.9×10^{-5} , 7.1×10^{-5} , 10×10^{-5} and 10×10^{-5} M for EO7, EO9, EO11 and EO14, respectively [26]. Measures of the volume of filtrate collected at different times were taken. The time scale varied with each series (as permeabilities differed between experiments) but it did not exceed 2000 s. To ensure that the comparison of the fluxes measured in different conditions was rigorously valid, the flux through the membrane with pure water was systematically checked between each two experiments with surfactants to ensure that there was no flux decline due to membrane fouling.

3.3. Determination of phenol content

Phenols were analyzed by UV using a SECOMAM S.750 spectrophotometer, France. Under the studied conditions, i.e. the acidity of the aqueous solutions, phenol and 4-nitrophenol were present in their neutral forms and they were analyzed at 270 and 318 nm, respectively. Linear correlations were obtained for the range of concentrations studied. The range of concentrations was 0.01–0.07 g l⁻¹ for phenol and 0.001–0.007 g l⁻¹ for 4-nitrophenol.

Continuous UV–VIS spectra were recorded using a SHIMADZU 215 spectrophotometer, Japan.

4. Results and discussion

Surfactants with average degrees of oxyethylation within 9 and 14 are substantially hydrophilic and contain negligible amounts of strongly hydrophobic homologues having up to three oxyethylene units. As a result, the cloud point of their solutions is high enough to avoid the clouding and separation of surfactant-rich phases. However, EO7 contains significant quantities of hydrophobic homologs and its cloud point is only slightly above the room temperature. The region of the isotropic micellar phase is broad (up to few tens percents) and viscous liquid-crystalline phases cannot form within the range of concentrations investigated. However, the clouding is possible and the hydrophobic components can precipitate or rather form surfactant-rich phase. The phenomenon should be considered rather as a gelation than as the precipitation because the surfactant-rich phase separates after several hours in the form of viscous drops. Taking the clouding phenomenon into account, EO9 surfactant is selected as the reference surfactant, although most of the experiments are also carried out for the other non-ionics, i.e. with different degrees of oxyethylation.

Fig. 2 demonstrates the effect of surfactant concentration on the collection of permeate. A linear relationship permeate volume versus time is obtained only for ultrafiltration of water. An addition of surfactant decreases the flux and the effect is stronger with a

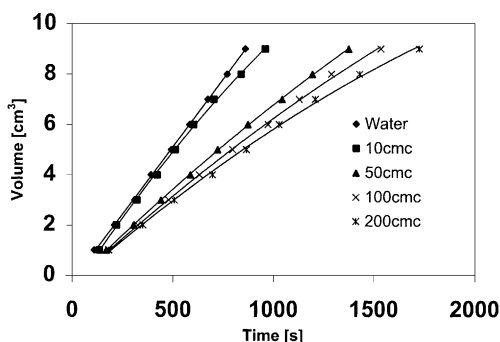


Fig. 2. Filtered volume as a function of time for OE9 micellar solution containing 4-nitrophenol ($C_{\text{NPH}} = 0.001 \text{ g l}^{-1}$).

decrease of the average degree of oxyethylation. The negative effect of surfactant concentration is strong in the region up to 50 cmc, and relatively small in the region up to 200 cmc.

The characteristic membrane coefficient was calculated as

$$K_{\text{mem}} = \frac{\mu_{\text{W}}}{\Delta P} v_{\text{A}} = 3 \times 10^{-7} v_{\text{A}} \quad (7)$$

where μ_{W} is the viscosity of water, from a reference series of experiments with water. Afterwards R_{SL} was calculated from Eq. (2). The calculation was performed using the cumulative volume permeated from time 0 to time t , and calculating the average flux. It was found that the averaged relationships obtained were much clearer than those which could be derived calculating resistance for the permeation of each incremental volume of fluid. The first result (Fig. 3) is that the relationship between average resistance and average flux is characteristic of each surfactant. The calculations to obtain R_{SL} from Eq. (2) have assumed that the permeating liquid has the viscosity of water (in all cases the viscosity of solutions with concentrations 100 times the cmc have been no more than 3% higher than water). From the figure it can be seen that R_{SL} between EO9 and the other surfactants are about 10–20% higher, which could not be explained by the assumption on viscosity being incorrect. Therefore, it is both necessary and feasible to obtain this information for each surfactant in order to model the average flux that will be achieved during a given run. Again it may be noticed that EO9 seems to exhibit a maximum

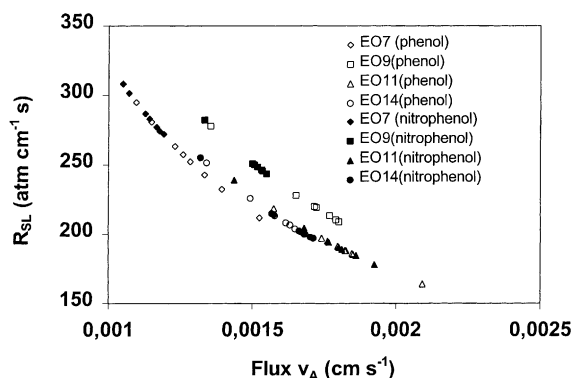


Fig. 3. Resistance due to the secondary layer vs. permeation flux (surfactant concentration into feed = 100 cmc).

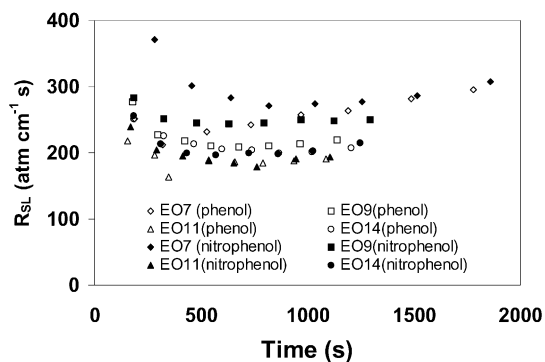


Fig. 4. Resistance due to the secondary layer vs. time (surfactant concentration into feed = 100 cmc).

resistance to a given flux: it increases from EO7 to EO9, and then decreases progressively to EO11 and EO14. Value of the K_S is 0.3233 for EO7, 0.3767 for EO9, 0.3433 for EO11, and 0.3367 for EO14 where K_S is defined by equation $R_{SL} = K_S/v$.

Fig. 4 shows that there is a significant influence of the pollutant present on the evolution of the resistance to permeation with time. In the presence of phenol, the surfactants with longer oxyethylene chains develop lower resistance. The longer chain oxyethylates tend to have resistance closer to that in the presence of nitrophenol. There is a tendency of the surfactants with phenol to “age” sooner and in the case of EO7 the effect is so dramatic that resistance equal

that with nitrophenol, although initially the resistance due to EO7/nitrophenol was twice larger. In general terms, there is an initial drop in resistance followed by a stabilization region and a subsequent (sometimes only hinted) build-up of resistance. The build-up of resistance seems to be linear.

Fig. 5 shows the relationship between the molar ratio bound phenol/micellar surfactant in the retentate and the pollutant concentration in the permeate. The micellar surfactant in the permeate is assumed to be the cmc of each surfactant. The calculation is

$$\Phi_{PH}^{Surf} = \frac{C_{PH}^{ret} - C_{PH}^{per}}{C_{Surf}^{ret} - C_{Surf}^{per}} \quad (8)$$

Again there are individual lines, almost straight, characteristic of each surfactant. This method of representing the amount of the pollutant removed is more useful than the calculation of rejection data from the point of view of modeling of an ultrafiltration unit, as thus, can be estimated a priori how much pollutant will be removed with a given surfactant concentration. For the surfactant used in this study, the correlations are

$$\begin{aligned} \Phi_{PH}^{EO7} &= 0.1734C_{PH}^{per} + 0.005 \\ \Phi_{PH}^{EO9} &= 0.1532C_{PH}^{per} + 0.004 \\ \Phi_{PH}^{EO11} &= 0.1048C_{PH}^{per} + 0.002 \\ \Phi_{PH}^{EO14} &= 0.1028C_{PH}^{per} + 0.004 \end{aligned} \quad (9)$$

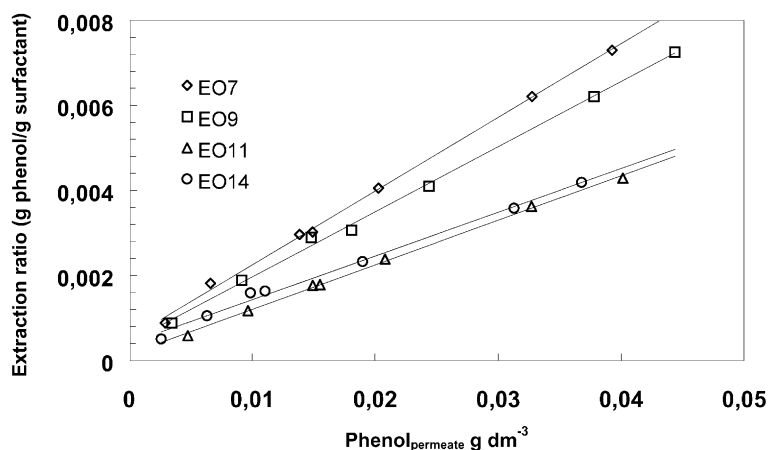


Fig. 5. The weight ratio between pollutant (phenol) and the various surfactants bound together in the micelles, and the free phenol concentration in equilibrium (surfactant concentration into feed = 100 cmc).

Knowing the relationship between surfactant concentrations in the feed and permeate, and the relationship between bound and free pollutant, it is therefore, possible to calculate a priori the surfactant type and feed concentration required to remove a given pollutant concentration. The small difference in the slope value between EO11 and EO14 suggests that the difference in weight of pollutant per unit weight of surfactant between the various homologues is not connected with the fraction of hydrophobic chain. There is a weaker difference between EO11 and EO14 than between EO9 and EO11, but the difference between the latter is stronger, than between EO7 and EO9. The result suggests that there is some barrier effect caused by the polar oxyethylated chains which opposes penetration of phenol towards the micellar core. Rejection factors were in general low, between 26 and 62%.

The results presented agree well with the data on solubilization available in the literature. The solubilization of hydrophilic solutes like the phenols investigated here increases with an increase of the polyoxyethylene chain up to the average degree of oxyethylation equal to 8–10 as such solutes are solubilized mainly between polyoxyethylene chains, rather near a hypothetical micelle interface. The effect disappears for more hydrophilic surfactants or a maximum solubilization is even observed for $n = 8$ –10 [27–29]. This limits the range of useful surfactants to a narrow range of oxyethylation degree.

Fig. 6 shows the effect of surfactant concentration on the resistance to permeation. As described in the literature, higher surfactant concentrations may lead to substantial surfactant–membrane interactions.

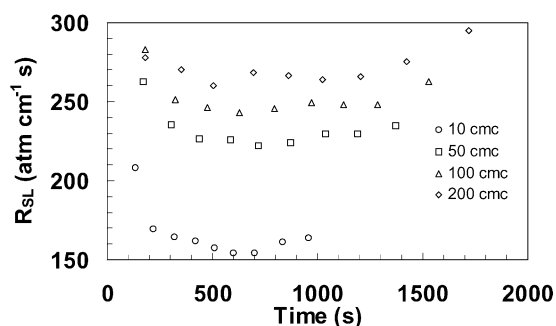


Fig. 6. The effect of surfactant (EO9) concentration in the feed on the evolution of resistance with time.

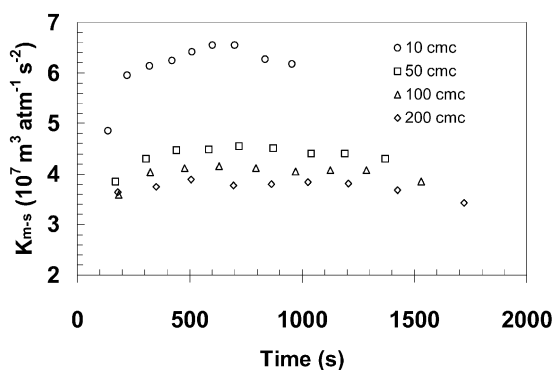


Fig. 7. A “pseudo-membrane coefficient” for EO9 vs. time.

In particular, it is interesting to see that there is a substantial difference between the resistance in the case of a solution with 10 times the cmc, and higher surfactant concentrations. Two more interesting facts observed in this figure are: (1) at shorter times the resistance is higher for higher surfactant concentrations in the feed; (2) the decline of the resistance is steeper for the lower surfactant concentrations in the feed; (3) the time to achieve the stabilization in the secondary resistance is shorter for the lower surfactant concentration in the feed.

Fig. 7 shows the values for EO9 of an analogous of the membrane coefficient K_{mem} . It has been calculated assuming that the viscosity of the “solution” going through the surfactant layer is that of the feed, with concentrations between 10 and 100 times the cmc, and therefore, that $K_{m-s} = \mu_{Feed}/R_{SL}$. The results indicate that the constant for 10 cmc (0.42 g l^{-1}) is much higher (the solution is much more permeable). The other solutions are closely grouped, and in the four cases there is an initial growth of the permeability, and a subsequent decrease. Considering together all the information, the results indicate that the concentration polarization effect is fast and takes place in a very short time. These also suggest that some sort of “permeabilisation” occurs as a consequence of the flow through the secondary layer. The “permeabilisation” effect is probably connected with the structure of the secondary layer (i.e. actual mesophase deposited). After a given period during which the secondary layer is deformed, which is longer when the concentration of surfactant is higher, there is a period of stabilization and then a decrease.

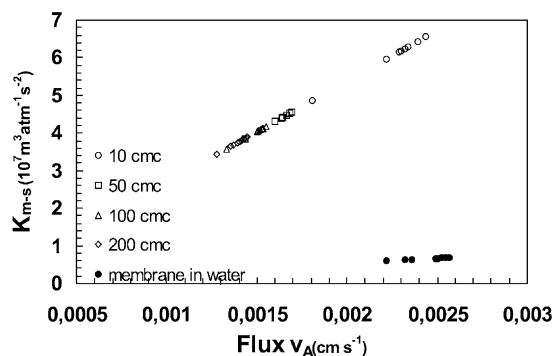


Fig. 8. The “pseudo-membrane” coefficient and the membrane coefficient vs. permeation flux for EO9.

Derived from Fig. 7, Fig. 8 shows that there is a linear relationship between the value of K_{m-s} and the permeation flux, exactly as it happens between K_{mem} and permeation flux (which is plotted as a reference as the series of black dots) within the experimental range and in the absence of surfactant. K_{m-s} is equal to $3 \times 10^{-6} v_A$, at least for v_A above 0.001 m s^{-1} , and the slope is one order of magnitude larger than that for K_{mem} in Eq. (7).

A last result of interest is found in Fig. 9, which shows the effect of pollutant concentration on the evolution of the resistance. The pollutant is phenol and the surfactant, again EO9. In general terms, there is a very small effect, except locally at the beginning, where it can be seen that the initial resistance is higher at higher phenol concentrations.

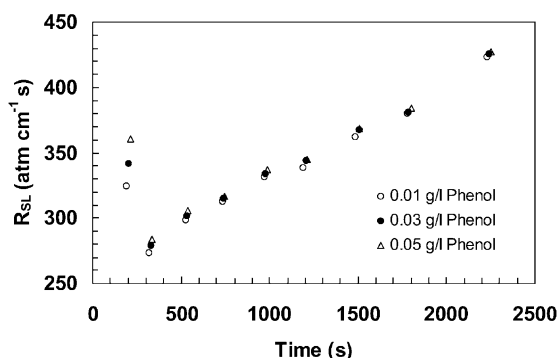


Fig. 9. Influence of pollutant concentration on the resistance EO9, at 4.03 g l^{-1} (i.e. 100 times of its cmc).

5. Conclusion

The build up of resistance due to concentration of the surfactant over the membrane takes place in a very short time. Afterwards, the membrane apparently re-orders itself due to the effect of the permeating solution and this increases its permeability until equilibrium is reached. After some time, the tendency is reverted and the membrane begins to loose permeability. The resistance opposed by the surfactant to the permeation flux is a characteristic function of the surfactant. The relationship between flux and resistance is independent of factors like surfactant concentration or the presence and concentration of pollutants. The evolution of resistance to permeation with time does depend on surfactant concentration and the chemical nature of pollutants. The effect of pollutant concentration, investigated in the case of phenol, is only observed during the initial build-up of resistance due to polarization concentration and the “permeabilisation” stage, where the resistance for the various pollutant concentrations converges to the same equilibrium value.

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